

Title: Analysis of Polycyclic Aromatic Hydrocarbons in Utility Ash
Using Modified California Air Resources Board Method 429

Author: Robert S. Mitzel
Phone: 916 933-1640
Fax: 916 933-0940
Alta Analytical Laboratory, Inc.
5070 Robert J. Mathews Parkway
El Dorado Hills, CA 95760

ABSTRACT

The purpose of this study is to develop an analytical method for determining the PAH (polycyclic aromatic hydrocarbons) content in fly ash.

This material has properties which can bind up the organic compounds and make extracting of these compounds from the matrix very difficult. Conventional methods, such as, EPA Method 8270 are well-known, however they are very limited in determining if the actual PAH compounds (particularly the high boiling compounds such as benzo(a)pyrene) are being successfully extracted out of the matrix.

In 1985 early developments of a PAH method for extracting these compounds from stack incinerators was developed in cooperation with the California Air Resources Board. Adopted in 1988, this method identified 19 PAH compounds using as isotope dilution technique and analyzing the compounds using a High Resolution Mass Spectrometer.

This presentation will demonstrate that with some minor modifications to this method successful determination of PAH compounds in the Fly Ash material can be achieved.

Introduction

CARB 429 was developed in the State of California for the analysis of PAH compounds from stack incinerators. It is Modified Method 5 procedure which uses XAD-2 traps, filters, and impingers referred to as the train. Connected on one end is a probe line which is located directly into the stack gas exhaust. The other end has a pump which pulls the stack gas exhaust through the train. The sample, once collected, is extracted using an isotope dilution technique where 15 labelled internal standard compounds are spiked into the sample prior to soxhlet extraction with methylene chloride. The extract is analyzed on a High Resolution Gas Chromatograph/High Resolution Mass Spectrometer at a resolution of 10,000 for 19 PAH compounds which comprises the CARB 429 list.

There has recently been an interest in determining the PAH content in the Fly Ash material. The properties of the Fly Ash required that the CARB 429 method would need modifications in order to successfully extract any possible compounds that may be present in the material.

In cooperation with the Pittsburgh Energy Technology Center, four distinct fly ash samples were sent to the laboratory for PAH characterization.

Preliminary work performed on one of the Fly Ash samples indicated that the use of Methylene Chloride as an extraction solvent did not result in acceptable recoveries of the internal standards spiked prior to extraction. Further work was performed with this material using four different solvents (methanol, methylene chloride, hexane and toluene) for soxhlet extraction.

Acceptable results were found using toluene refluxing in a soxhlet extractor for 16 hours.
(See Table I.)

The four samples were set up for soxhlet extraction using toluene. In addition to the four samples, one of the samples was selected to perform a matrix spike/matrix spike duplicate (MS/MSD). Approximately 5.0 grams of each sample was weighed out and placed in a thimble. The internal standard mix was introduced directly into each sample. The MS/MSD samples also had a known concentration of the 19 PAH compounds added. Additional QC for these samples included a method blank and a pair of Laboratory Control Samples (LCS's). LCS samples are method blanks spiked with native PAH compounds to assess overall precision and accuracy of the method.

Result

(See Table II.)

Trace levels of PAH compounds were present in all four samples from naphthalene to pyrene. Two of the samples had low levels of benz(a)anthracene and chrysene, and one sample had low levels of benzo(b)fluoranthene. Internal standard recoveries were all within acceptable ranges or met the signal-to-noise criteria specified in CARB 429. The MS/MSD performed on one of the samples showed very good recoveries for the native PAH compounds ranging from 65% to 145% with the average recovery of 113% and an average relative percent difference of 5.7%. The internal standard recoveries were within acceptable limits with an average recovery of 74%.

Conclusion

Isotope dilution techniques such as the one used to perform this study are very useful analytical procedures for calculating concentrations of compounds in various matrices. Although, further work needs to be done, these preliminary findings indicate that this modified version of CARB Method 429 can be a useful tool in measuring the levels of PAH compounds in Fly Ash material.